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Preliminary communication

Reaction of zirconium hydrocarbyls with carbon monoxide

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SUMMARY

Carbon monoxide reacts with tetrahydrocarbylzirconium compounds, $(RCH_2)_4Zr$, where R = phenyl or vinyl to give a polymeric species containing Zr–O–C bonds, which on hydrolysis yields products consistent with successive insertion of CO and $ZrC(=O)CH_2R$ into the Zr–C bonds.

When carbon monoxide is passed through a solution of zirconium tetrabenzyl in decalin at 22° and atmospheric pressure under nitrogen, the solution slowly discolours and a white precipitate is formed. This insoluble material has been characterised as an organozirconium polymer (C, 43.0; H, 4.75; Zr, 33.2) containing Zr–O–C bonds, but no $Zr \leftarrow CO$, $Zr–CO–CH_2R$* or residual π-allyl groups. Hydrolysis of the product mixture gave two volatile products, which were quantitatively separated by GLC and liquid column chromatography. These were identified by ^{1}H NMR, infrared and mass spectroscopy as 2-benzyl-1,3-diphenyl-1-propene (VIII, R = phenyl), 17% and 2-benzyl-1,4-diphenyl-3-butanone (VI, R = phenyl), 5%. One of three minor products was identified as dibenzylketone, ca. 1%.

In the analogous reaction of carbon monoxide with tetraallylzirconium in chlorobenzene, the deep red solution rapidly becomes a golden yellow and a white solid slowly deposits (C, 49.7; H, 7.6; Zr, 22.3). However, in this case hydrolysis yielded only one identifiable organic product, which was characterised as 5-allyl-1,3,7-octatriene-4-ol (V, R = vinyl).

These results are consistent with the reaction sequence shown in Fig. 1. Initial insertion of CO into the Zr–C bond is followed by rapid secondary reaction, involving either insertion of the acyl carbonyl into another Zr–C bond to form I or by elimination

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*The formation of stable acyltitaniums, $Cp_2Ti(COR)Cl$, has been reported[1] very recently.

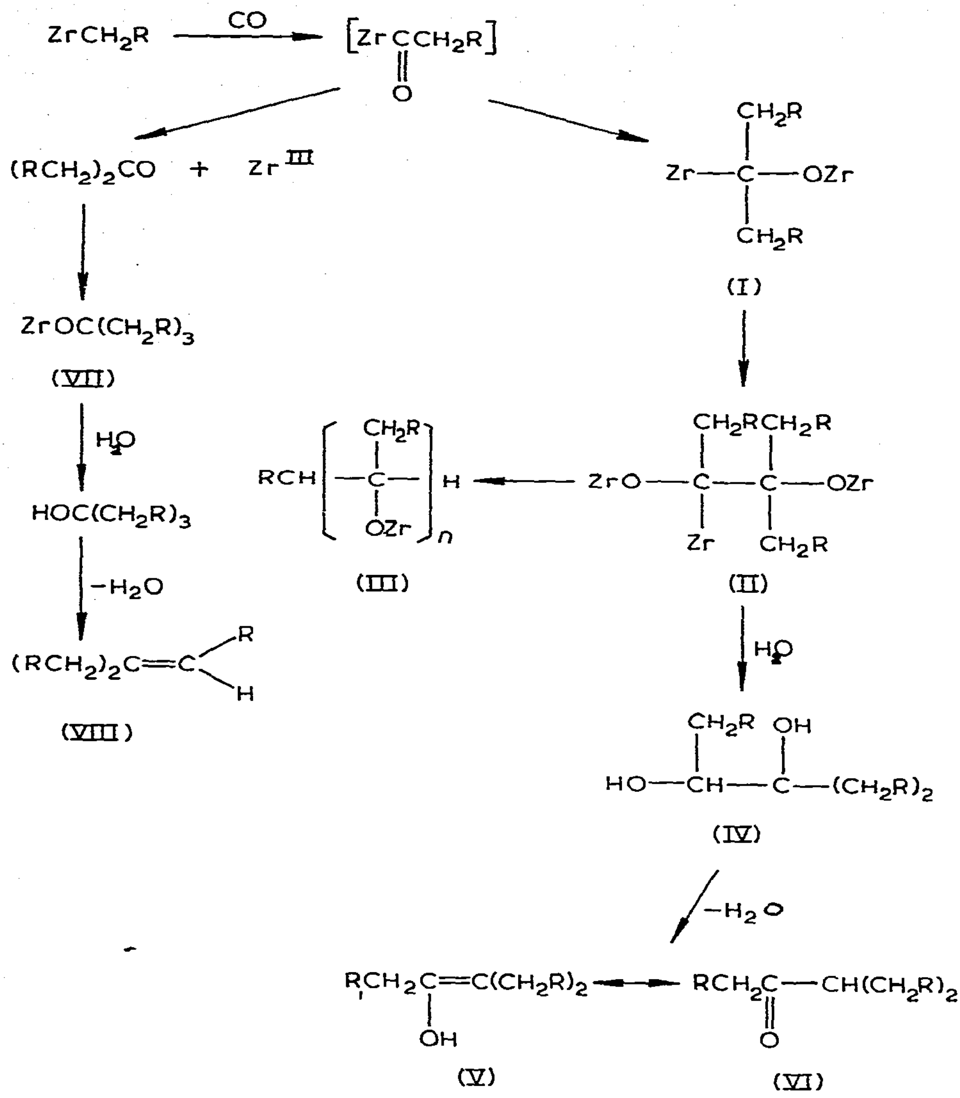

Fig. 1. Sequence of carbon monoxide reaction with Zr–C bonds. Zr denotes Zr^{IV} with four covalently bonded substituents.

to give a ketone. Repetition of the sequence of CO and $>C=O$ insertion into Zr–C bonds leads to oligomeric, II, and polymeric, III, products, consisting primarily of $(RCH_2\overset{|}{\underset{|}{C}}-O-Zr)$ units. Hydrolysis of II gives the diol, IV, which by dehydration forms the observed products VI (R = phenyl) and V (R = vinyl). Further reaction of the ketone (R = phenyl) by insertion into a Zr–C bond forms VII, which by hydrolysis and dehydration yields the observed product VIII (R = phenyl).

The ease with which the acylmetal undergoes further reaction with Zr–C bonds, contrasts with the relative stability of the acyl derivatives of Group VIII transition metals and is similar to the observed reactions of main group metal–carbon bonds (*e.g.* magnesium[2]) with CO and ketones. Likewise the elimination of dibenzylketone parallels the formation of ketones in the reaction of CO with alkyl- and aryl-lithiums. However the results do clearly reflect the high affinity of Group IVA metals for oxygen.

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